Available online at www.sciencedirect.com

Catalysis Today 101 (2005) 203–210

www.elsevier.com/locate/cattod

Solar photocatalytic degradation and detoxification of EU priority substances

M. Hincapié [b,1], M.I. Maldonado [a], I. Oller [a], W. Gernjak [a], J.A. Sánchez-Pérez [c], M.M. Ballesteros [c], S. Malato [a,*]

[a] *Plataforma Solar de Almería-CIEMAT, Carretera Senés km4, 04200 Tabernas (Almería), Spain*
[b] *Facultad de Ingeniería Ambiental, Universidad de Medellín, Carrera 87 No. 30-65, P.O. Box 1983, Medellín, Colombia*
[c] *Departamento de Ingeniería Química, Universidad de Almería, Crta de Sacramento s/n, 04120 Almería, Spain*

Abstract

Several different pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) considered PS (priority substances) by the European Commission and dissolved in water at 50 mg/L (or at maximum water solubility) have been degraded at pilot-plant scale using photo-Fenton and TiO_2 photocatalysis driven by solar energy. Two different iron concentrations (2 and 55 mg/L) and TiO_2 at 200 mg/L have been tested and discussed, using mainly TOC mineralisation for comparison of treatment effectiveness. *Vibrio fischeri* (Microtox®) toxicity assays were also employed for evaluating the photocatalytic treatments, and comparison between these results and parent compound disappearance, TOC evolution and anion (or ammonia) release were discussed. Almost complete mineralisation and total detoxification were always attained. It has been demonstrated that evolution of chloride could be a key-parameter for predicting toxicity of chlorinated compounds.

Keywords: Advanced oxidation treatment; Pesticide degradation; Photocatalysis; Photo-Fenton; Toxicity evolution; Wastewater treatment

1. Introduction

EU legislation is continually adapted to protect and improve the quality of Europe's fresh water resources. The most recent update was the European Water Framework Directive WFD, Directive 2000/60/EC, establishing a framework for Community action in the field of water policy. The WFD presents a breakthrough in EU water policy, not only with respect to the scope of water protection, but also its development and implementation. The WFD establishes a framework for the protection of inland surface, transitional and ground water, and aims to achieve good ecological potential and chemical condition of surface water by 15 years from the date the Directive became effective (22 December, 2000), at the latest. The WFD lays the EU water pollution strategy, including a list of 33 priority substances (PS), which represent a significant risk to or via the European aquatic environment. Several water-soluble pesticides are included among these substances: alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol (of special interest because of their extremely easy transport in the environment, seriously threatening all surface and groundwater).

The processes and technologies available at the present time for the treatment of polluted water are varied [1,2]. The wastewater treatment techniques most frequently used can be divided into physical, biological and chemical. Urban wastewater is usually only treated with physical and biological techniques, which greatly reduce the pollution, but not enough to comply with current standards, which are becoming stricter, as mentioned above. The tendency is toward greater use of chemical treatment, both to comply with standards and to recycle used water more, which is the great goal for the future. Moreover, wastewater-containing pesticides can very often not be treated by biological techniques, since they are toxic for the microorganisms and therefore their biodegradation is impossible.

---

[*] Corresponding author. Tel.: +34 950387940; fax: +34 950365015.
E-mail address: sixto.malato@psa.es (S. Malato).

[1] PhD student of GIGA (Universidad de Antioquia, Colombia).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.004

This work focuses on a technology designed to help solve this type of non-biodegradable toxic compound treatment problem. In the near future, advanced oxidation processes (AOPs) may become the most widely used water treatment technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability [3–5]. These processes involve generation and subsequent reaction of hydroxyl radicals ($^{\bullet}OH$), which are the most powerful oxidizing species after fluorine. Many oxidation processes, such as TiO_2/UV, H_2O_2/UV, photo-Fenton and ozone (O_3, O_3/UV, O_3/H_2O_2) are currently employed for this purpose. Their attack is not very selective, which is a useful attribute for use in pollution treatment. The versatility of AOPs is also enhanced by the fact that there are different $^{\bullet}OH$ radical production possibilities, so they can be adapted to specific treatment requirements. Their main disadvantage is their high cost.

The use of AOPs for wastewater treatment has been studied extensively, but UV radiation generation by lamps or ozone production is expensive. Therefore, research is focusing more and more on those AOPs which can be driven by solar radiation, i.e., light with a wavelength longer than 300 nm: photo-Fenton and heterogeneous catalysis with UV/TiO_2 [6,7]. This work evaluates these two well-defined AOP systems in a large pilot plant. The processes were applied to the degradation of the six pesticides considered PS by the WFD as mentioned above. The efficiency of both treatment methods was evaluated not only for pesticide degradation and mineralisation, but also water toxicity at different stages of treatment.

2. Experimental

2.1. Chemicals

Alachlor (95% technical grade $C_{14}H_{20}ClNO_2$, Aragonesas Agro S.A.), atrazine (95%, technical grade $C_8H_{14}ClN_5$, Ciba-Geigy), chlorfenvinphos (93.2%, technical grade $C_{12}H_{14}Cl_3O_4P$, Aragonesas Agro S.A.), diuron (98.5%, technical grade $C_9H_{10}Cl_2N_2O$, Aragonesas Agro S.A.), isoproturon (98%, technical grade $C_{12}H_{18}N_2O$, Aragonesas Agro S.A.) and pentachlorophenol (98%, analytical grade C_6HCl_5O, Aldrich Chemical) were used as received. Analytical standards of all pesticides (for chromatographic analyses) were purchased from Sigma–Aldrich. Water used in the pilot plant was obtained from the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10 μS/cm, $Cl^- = 0.7$–0.8 mg/L, organic carbon < 0.5 mg/L). Iron sulphate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide (30%, w/v) and sulphuric acid for pH adjustment (around 2.7–2.8) were reagent grade. TiO_2 was Degussa P-25.

2.2. Analytical determinations

Mineralisation was followed by measuring the total organic carbon (TOC) by direct injection of filtered samples into a Shimazu-5050A TOC analyser provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. Pesticide concentration was analysed using reverse-phase liquid chromatography (flow 0.5 mL min^{-1}) with UV detector in a HPLC-UV (Agilent Technologies, series 1100) with C-18 column (LUNA 5 μm, 3 mm × 150 mm, from Phenomenex). Ultra pure distilled-deionized water obtained from a Milli-Q (Millipore Co.) system and HPLC-grade organic solvents were used to prepare all the solutions. Cation concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm × 250 mm column. Isocratic elution was done with H_2SO_4 (10 mM) at a flow rate of 1.2 mL min^{-1}. Anion concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. The gradient programme was pre-run 5 min with 20 mM NaOH, injection, 8 min 20 mM NaOH and 7 min NaOH 35 mM, flow rate 1.5 mL min^{-1}. H_2O_2 concentration was determined by iodometric titration.

2.3. Toxicity evaluation

A commercial assay marketed as Microtox® was used. The reagent is a freeze-dried preparation of a specially selected strain of the marine bacterium *Vibrio fischeri* (formerly known as *Photobacterum phosphoreum*, NRRL number B-11177). To monitor the inhibition, different dilutions of the test sample, made with a specially prepared non-toxic 2% sodium chloride solution, were mixed with the bacterial suspension. The drop in light emission was measured after contact periods of 5 and 15 min. Hydrogen peroxide present in the samples from photo-Fenton experiments was removed prior to toxicity analysis using catalase (2500 U/mg bovine liver; 100 mg/L) acquired from Fluka Chemie AG (Buchs, Switzerland) after adjusting the sample pH to 7.

Careful control of temperature was essential because light emission is sensitive to temperature. For example, for *P. phosphoreum* the light intensity changes by about 10% for every °C variation in temperature. Light production from luminescent bacteria was measured with a SDI Microtox® Model 500 Analyzer, at the optimum test temperature of 15 °C. The inhibition effect of the samples was compared with a toxicant-free control to obtain percent inhibition (INH %)

$$\mathrm{INH}\,(\%) = \left(\frac{\Gamma}{1+\Gamma}\right) \times 100 \qquad (1)$$

where the gamma function expresses the ratio of light lost to light remaining, and is calculated as follows:

$$\Gamma = \left(\frac{R \times I_0}{I_t}\right) - 1 \qquad (2)$$

where I_0 and I_t are the luminescence intensities of the sample at the beginning and after the contact time, respectively, and R the correction factor for the control

$$R = \frac{I_{C_t}}{I_{C_0}} \qquad (3)$$

where I_{C_0} and I_{C_t} are the luminescence intensities of the control initially and after contact time, respectively.

2.4. Experimental set-up

All the experiments were carried out under sunlight, in a pilot plant at the PSA (latitude 37°N, longitude 2.4°W). The pilot plant operates in batch mode and has three compound parabolic collectors (CPCs), one tank and one recirculation pump. Each collector (1.03 m^2 each) is mounted on a fixed platform tilted 37° (local latitude). The water flows at 20 L/min directly from one module to another and finally into the tank, from which the pump recirculates the fluid back to the CPCs. The total volume (V_T) of 35 L is separated into two parts: 22 L (glass-transparent tubes in the CPC) of total irradiated volume (V_i) and the dead reactor volume (tank + high density polyethylene tubes), which is not illuminated, as recently described in detail elsewhere [8]. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3), mounted on a platform tilted 37° (the same as the CPCs), which provides data in terms of incident $W_\mathrm{UV}\ \mathrm{m}^{-2}$. In this way, the energy reaching any surface in the same position with regard to the sun can be measured. With Eq. (4), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible.

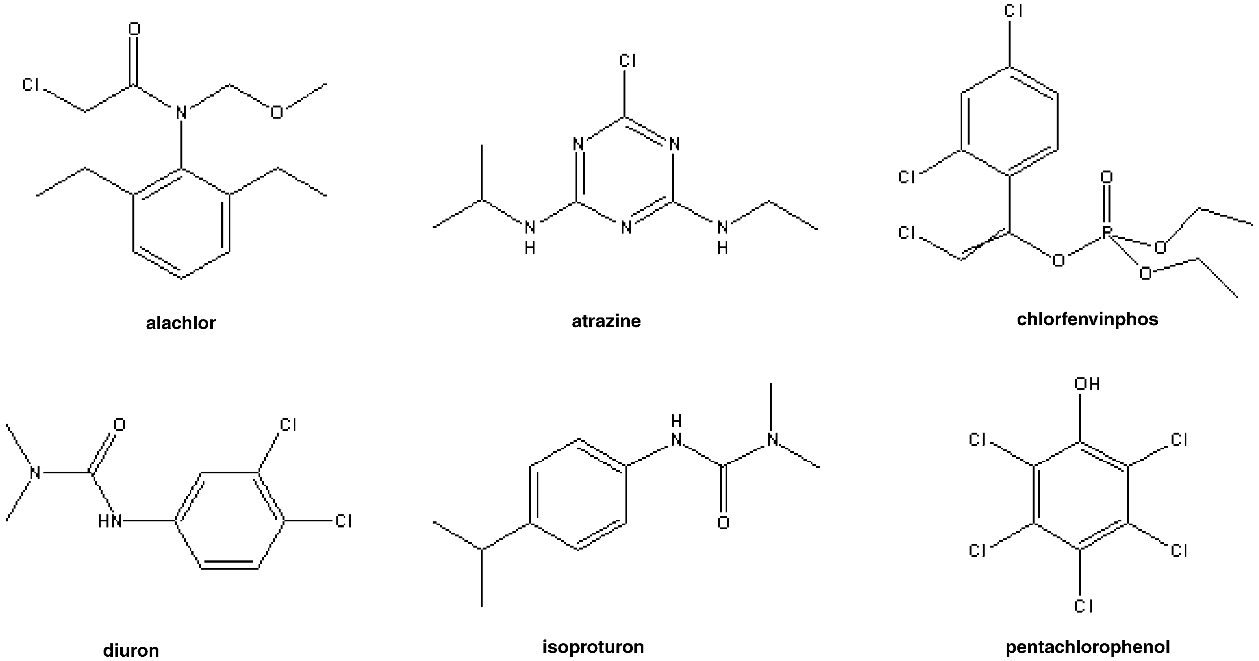
$$t_{30\,\mathrm{W},n} = t_{30\,\mathrm{W},n-1} + \Delta t_n \frac{\mathrm{UV}}{30}\frac{V_\mathrm{i}}{V_\mathrm{T}}, \quad \Delta t_n = t_n - t_{n-1} \qquad (4)$$

where t_n is the experimental time for each sample, UV the average solar ultraviolet radiation measured during Δt_n, and $t_{30\,\mathrm{W}}$ the "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon). As the system is outdoors and is not thermally controlled, the temperature achieved inside the reactor is continuously recorded by a PT-100.

The characteristics (mainly water solubility) of the six pesticides tested (Scheme 1), made the use of "simulated wastewater" preparation procedures necessary The alachlor, chlorfenvinphos and isoproturon solutions were prepared mixing for several hours to achieve a 50 mg/L concentration in the pilot plant. Atrazine, diuron and pentachlorophenol are soluble in water at less than 50 mg/L at ambient temperature. In order to test them at the maximum initial concentration, a saturated solution was prepared in the auxiliary 100 L-tank and mixed for a further 24 h. Then the pilot plant was completely filled with water from the auxiliary tank, avoiding the transfer of any undissolved solids.

3. Results and discussion

The main parameters used to monitor the degradation and mineralisations of each pesticide tested in this work were TOC and toxicity (measured as % of inhibition). In some cases, inorganic species produced (mainly chloride, nitrate and ammonia) and pesticide concentrations were used as indicators. Several points concerning the test results are common to all the pesticides and can be discussed together. For instance, mineralisation (i.e., disappearance of TOC) was attained only after irradiation with 2 mg/L iron, but significant mineralisation was also attained during "dark Fenton" with 55 mg/L iron. No degradation has ever been detected with TiO_2 in the dark.



Scheme 1. Chemical structure of pesticides tested.

The main objective of the first set of experiments was to find the best Fe concentration for comparison with TiO_2 (and for evaluating toxicity with both phototreatments, as the next step). Two very different Fe concentrations (2 and 55 mg/L) were selected. According to previous results with other compounds [9,10], small amounts of iron could well be enough to provide satisfying reaction rates. Furthermore, 1 mM Fe has very often been used as the maximum concentration [5,11,12], because up to this value the photons are absorbed only in the outer part of the photoreactors. Fig. 1 shows these results. All the experiments were done in the same way. Once the pesticide dissolved in water had been added to the pilot plant, it was homogenised in the system. Then a sample was taken (initial concentration, Point 1) and sulphuric acid was added. After another 15 min a second sample was taken (Point 2) and a pH of around 2.7–2.8 was confirmed. After that, iron salt ($FeSO_4.7H_2O$) was added and mixed for 15 min (Point 3). Finally, the necessary amount of hydrogen peroxide was added, and after 15 min a sample was taken to evaluate the dark Fenton reaction ($t_{30\,\mathrm{W}} = 0$). At that moment collectors were uncovered and the photo-Fenton experiments began. In the case of pentachlorophenol, acid was not added to avoid precipitation, but pH evolved very quickly to acidic pH (due to release of chloride) and photo-Fenton was effective (no Fe precipitation was detected).

As shown in Fig. 1, the mineralisation rate using 2 mg/L of iron was in most cases lower than with 55 mg/L of iron. All the parent compounds were very quickly completely degraded, with a very similar degradation rate at both Fe concentrations. The main difference was related to the "dark" Fenton reaction, which always produces significant

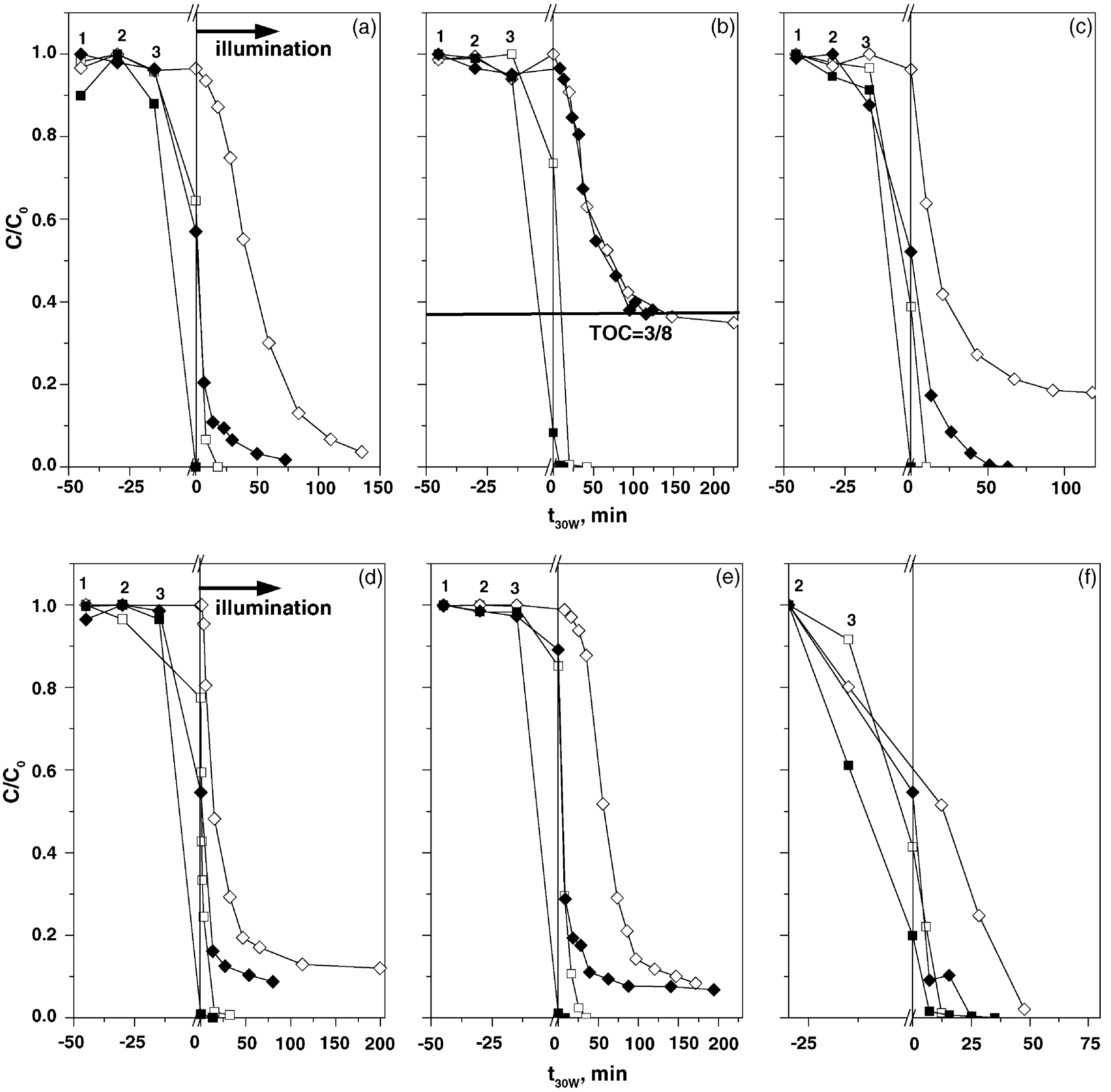


Fig. 1. Degradation by photo-Fenton of all compounds tested at two different iron concentrations: (a) alachlor, (b) atrazine, (c) chlorfenvinphos, (d) diuron, (e) isoproturon and (f) pentachlorophenol. TOC 3/8 line for atrazine represents the non-degradable triazine ring. Points 1, 2 and 3 refer to the different steps in the procedures applied prior to illuminating the system (see text for details). (□) Pesticide, Fe 2 mg/L; (■) pesticide, Fe 55 mg/L; (◇) TOC, Fe 2 mg/L; (◆) TOC, Fe 55 mg/L.

disappearance of the pesticide, but very slight mineralisation (TOC decrease) before illumination. The mineralisation rate after illumination was quite similar in all cases. Under these circumstances, it was demonstrated that photo-Fenton at low iron concentrations is a suitable treatment because: (i) 2 mg/L of Fe are enough for mineralising the pesticides (ii) the mineralisation with 2 mg/L of Fe did not occur until the water was illuminated, (iii) the mineralisation rate under illumination was very similar between 2 and 55 mg/L. Chloride analyses (determined during degradation of chlorinated compounds) showed very fast degradation/dechlorination compared to disappearance of TOC. Therefore, residual TOC remaining in the water at the end of some experiments did not correspond to any chlorinated compound. This dechlorination usually also provokes a decrease of toxicity. In several cases, total mineralisation was difficult to reach; meaning that the intermediates formed at the end of the treatment are more resistant, and it could be uneconomical (due to the heavy hydrogen peroxide consumption under these conditions) to continue treatment. Under these circumstances, monitoring of water toxicity before total mineralisation is more than justified to stop the AOP treatment after detoxification requirements are attained.

In Fig. 2, it may be observed that in all cases photo-Fenton is quicker than TiO_2 (this is discussed in detail

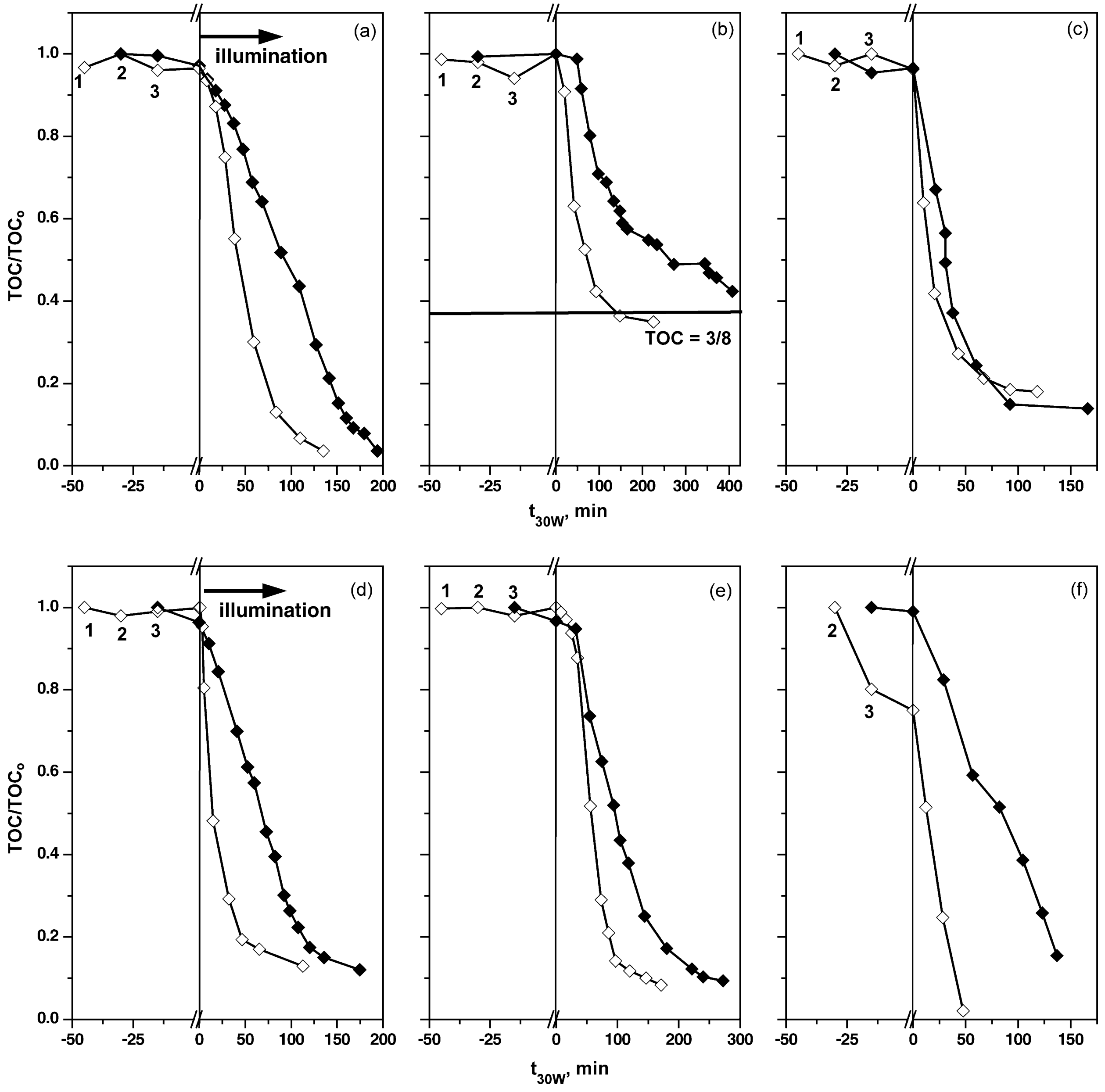


Fig. 2. Mineralisation by photo-Fenton and TiO_2 of tested compounds: (a) alachlor, (b) atrazine, (c) chlorfenvinphos, (d) diuron, (e) isoproturon and (f) pentachlorophenol. TOC 3/8 line for atrazine represents the non-degradable triazine ring. Points 1, 2 and 3 refer to the different steps in the procedures applied in photo-Fenton tests prior to illuminating the system (see text for details). (◇) TOC, Fe 2 mg/L; (◆) TOC, TiO_2 200 mg/L.

below). PCP is mineralised by photo-Fenton more quickly than the other compounds, which is not unusual because chlorophenols are very easily degraded by this AOP. Note that "dark" Fenton is very efficient with only 2 mg/L of Fe. On the other hand, atrazine is not completely mineralised because it is well-known that triazines cannot be mineralised until the end by photocatalysis or photo-Fenton due to the stability of the triazine ring. Concerning inorganic species produced, it is worth mentioning that organic chlorine was recovered as dissolved chloride in all cases. A more detailed commentary is included in the discussion of toxicity. Ammonia and nitrate were detected in different relative concentrations, and total balance of N was obtained only in the case of alachlor, mainly as ammonia. The nitrogen mass balance of atrazine was unclear, considering that two N atoms would have to be mineralised (the other three atoms are contained in the ring). It has been described before [13] that in TiO_2 photocatalysis, Atrazine generates both NO_3^- and NH_4^+ at a concentration ratio of $NH_4^+/NO_3^- = 0.69$, ammonium ions being the precursors of nitrate. A similar ratio was found in this case. Behaviour of diuron and isoproturon was very similar. Around 10% of the initial TOC was difficult to degrade. This effect was unaffected by TiO_2 or photo-Fenton, which affected only the mineralisation rate.

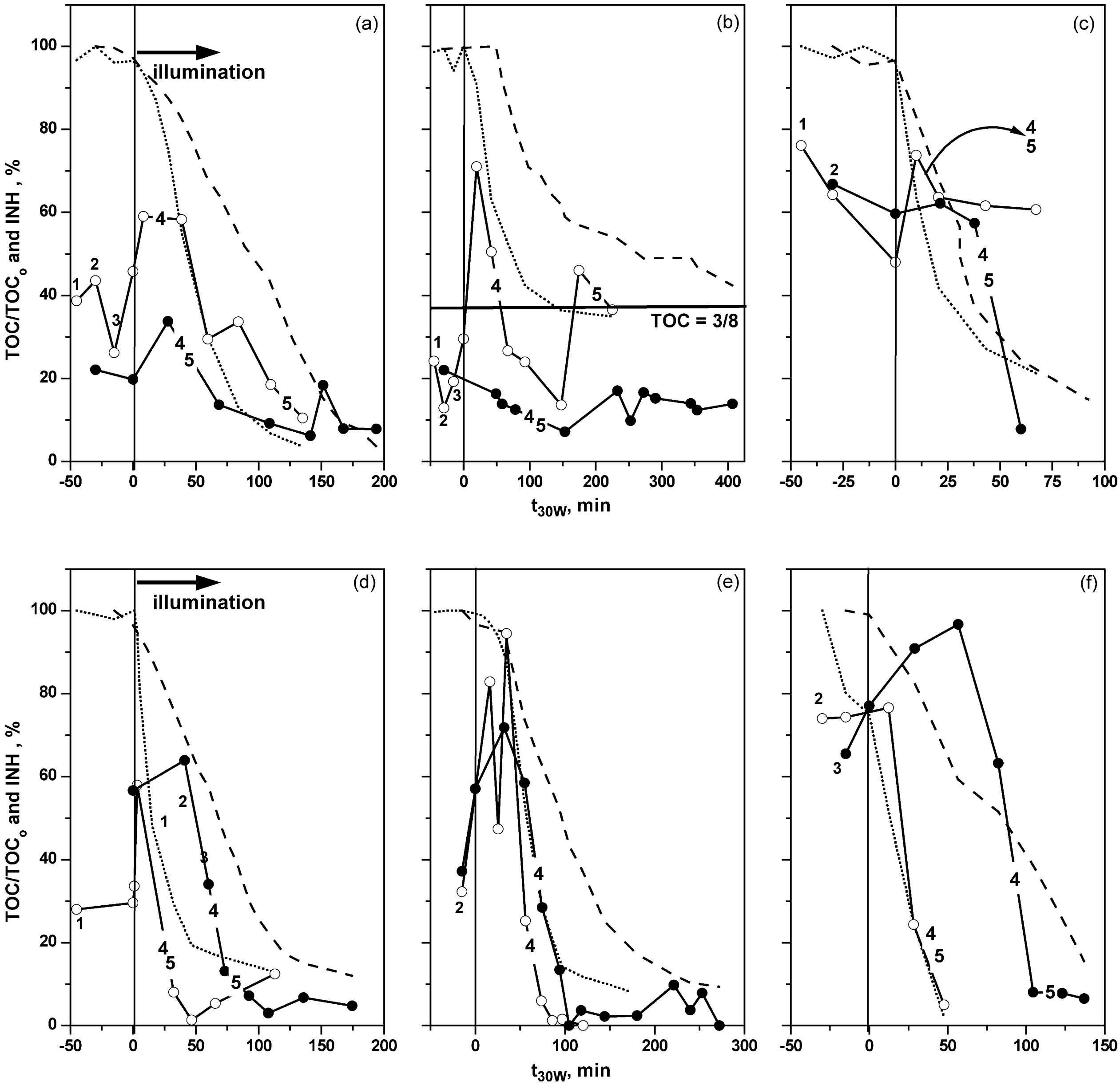


Fig. 3. Evolution of mineralisation and toxicity in compounds tested with photo-Fenton and TiO_2: (a) alachlor, (b) atrazine, (c) chlorfenvinphos, (d) diuron, (e) isoproturon and (f) pentachlorophenol. TOC 3/8 line for atrazine represents the non-degradable triazine ring. Points 1, 2 and 3 refer to the different steps in the procedures applied in photo-Fenton tests prior to illuminating the system (see text for details). (4) marks complete pesticide disappearance, and (5) marks organic chlorine recovery as dissolved chloride. (. . .) TOC, Fe 2 mg/L; (- - -) TOC, TiO_2 200 mg/L; (○) % inhibition, Fe 2 mg/L; (●) % inhibition, TiO_2 200 mg/L.

This TOC should correspond only to aliphatic compounds, as HPLC diode array detector scans did not show any signal above 210 nm. The very slow degradation of TOC from phenylurea pesticides after 80–90% mineralisation [14–16] and the very slow mineralisation of urea [17], which can be predicted as an intermediate of diuron and isoproturon, have also been previously reported. Urea contains only 1 C atom and 2 N atoms, which could justify not only the remaining 10% of the initial TOC, but also the incomplete release of N as NH_4^+ or NO_3^-. The results are very consistent with both pesticides and both treatments. When TOC is 10% of the initial, two atoms of N have still not been mineralised. The same is true of the toxicity results shown below. In the four cases (diuron and isoproturon by photo-Fenton and photocatalysis, respectively), toxicity is almost the same when TOC is 10% of the initial, predicting the presence in the treated water of the same type of compounds.

Proper toxicological evaluation of the complex reaction mixtures that originate at different stages of the photocatalytic degradation processes is not an easy task. The toxicity of these mixtures is difficult to predict, since the identity and concentration of each compound present in the samples are often unknown. Furthermore, the mechanism must be known by which both original compounds and their degradation products act, which is often impossible. Bioassays are experiments, normally performed in the laboratory, in which the toxic effects caused by certain pollutants are measured under controlled conditions [18]. The wide variety of bioassays that exist may be classified by the organism used for them, exposure time and concentration of the toxic agent [19]. Development and applications of biological toxicity are rapidly increasing. Today there are numerous bioassay procedures available, however, it is hard to establish the sensitivity of these assays and therefore, a universal monitoring device for toxicity assays is very unlikely. In any case, most recent studies have dealt with the use of luminescent bacteria tests for monitoring toxicity [20–22], and very often for the toxicity of pollutants to activated sludge. It has been demonstrated that the *V. fischeri* test was usually more sensitive than activated sludge [23,24] and this could be useful for assuring safe disposal of the water in a biological treatment plant and/or predicting biodegradability. The sensitivity of *V. fischeri* has also been evaluated in quite a few pesticides [25].

Fig. 3 shows the evolution of representative toxicity curves (% inhibition) for the bioassays performed during both treatments applied to the six pesticides. Chemicals added to the water for photocatalysis were removed prior to bioassay. TiO_2 was removed by filtration, H_2O_2 by quenching with catalase and iron by coagulation and filtration after neutralising the samples. Fig. 3 also shows the evolution of toxicity as a function of illumination time during degradation tests with TiO_2 and photo-Fenton. In this case, the experiments were extended until all toxicity bioassays showed inhibition below 50% or TOC mineralisation was significant (more than 90%).

Alachlor toxicity showed very similar behaviour in both treatments. Toxicity increased at the beginning of the treatment, but decreased sharply after total alachlor disappearance, but mainly when total chlorine was recovered as chloride. This reinforces the idea of formation of a chlorinated intermediate more toxic than the parent compound. So, in this case, to use total degradation of alachlor as a water disposal ‘‘control parameter’’ could be risky. Similar behaviour was detected in most of the other cases. It seems that more toxic compounds were formed during the first stages of the treatment and were then successfully degraded afterwards. Furthermore, in all cases except chlorfenvinphos with photo-Fenton in which a chlorinated pesticide was tested, toxicity was always shown to be low (inhibition of less than 20%) when total dechlorination was attained. Between the release of other inorganics (ammonia, nitrate, etc.) and toxicity evolution, no relationship has been observed. It also seems that at the same TOC during the first stages of the treatment, intermediates formed by the treatments were not exactly the same either. This means that TOC alone is an inadequate parameter for determining the efficiency of different photocatalytic methods, because for the same TOC, the toxicity is very different, although, when TOC was low enough, toxicity was almost the same.

4. Conclusions

One of the main objectives of this work was to demonstrate that detoxification of water containing pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) is possible without total mineralisation and in a reasonable time. This was demonstrated in all six cases.

Iron at very low concentrations could be enough for treating wastewater-containing pesticides. This could be very helpful because removal of iron at this concentration and before disposal would not be necessary. It has also been demonstrated that photo-Fenton was more efficient than TiO_2, not only for pesticide degradation but also for TOC mineralisation.

Pesticide metabolites may be more toxic than their parent compounds. This means that initial concentration of the parent compound and/or TOC cannot easily be correlated with toxicity. Toxicity was always reduced at the end of the treatment, but it was already quite low just after total dechlorination of the contaminant.

Acknowledgements

The authors wish to thank the European Commission for financial support under the CADOX Project (contract no. EVK1-CT-2002-00122). The authors also thank Mrs. Deborah Fuldauer for the correction of the English. Mr.

Gernjak would like to thank the Austrian Academy of Sciences for a DOC Programme grant. Mrs. Hincapié thanks the University of Medellín (Colombia) and GIGA (University of Antioquia) for financial support.

References

[1] M. Henze, P. Harremoës, J. La Cour Jansen, E. Arvin, Wastewater Treatment: Biological and Chemical Processes, 3rd ed. Springer-Verlag, Berlin, 2000.

[2] P. Wilderer, S. Wuertz, Modern Scientific Tools in Bioprocessing, Elsevier, Amsterdam, 2002.

[3] P.R. Gogate, A.B. Pandit, Adv. Environ. Res. 8 (2004a) 501.

[4] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B: Environ. 42 (2003) 319.

[5] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Appl. Catal. B: Environ. 47 (2004) 219.

[6] D. Bockelmann, R. Dillert, J. Dzengel, R. Goslich, E. Groß, M. Hilgendorff, D. Hufschmidt, R. Memming, G. Sagawe, M. Schober, H.-W. Schuhmacher, V. Selzer, U. Siemon, S. Vollmer, J. Theurich, D. Bahnemann, Solar Energy 77 (2004) 445.

[7] S. Malato, J. Blanco, A. Vidal, C. Richter, Appl. Catal. B: Environ. 37 (2002) 1.

[8] M. Kositzi, I. Poulios, S. Malato, J. Cáceres, A. Campos, Water Res. 38 (2004) 1147.

[9] A. Agüera, M. Mezcua, D. Hernando, S. Malato, J. Cáceres, A. Fernández-Alba, Int. J. Environ. Anal. Chem. 84 (2004) 149.

[10] A.R. Fernández-Alba, D. Hernando, A. Agüera, J. Cáceres, S. Malato, Water Res. 36 (2002) 4255–4262.

[11] P.R. Gogate, A.B. Pandit, Adv. Environ. Res. 8 (2004) 553.

[12] G. Sagawe, A. Lehnard, M. Lübber, D. Bahnemann, Helv. Chem. Acta 86 (2001) 3742.

[13] G.K.-C. Low, S.R. McEvoy, R.W. Matthews, Environ. Sci. Technol. 25 (1991) 460.

[14] V. Maurino, C. Minero, E. Pelizzetti, M. Vincenti, Colloid Surf. A: Phys. Eng. Asp. 15 (1999) 329.

[15] M. Muneer, J. Theurich, D. Bahnemann, Res. Chem. Int. 25 (1999) 667.

[16] S. Parra, J. Olivero, C. Pulgarín, Appl. Catal. B: Environ. 36 (2002) 75.

[17] P. Maletzky, R. Bauer, Chemosphere 37 (1998) 899.

[18] D.J. Paustenbach, J. Toxicol. Environ. Health B 3 (2000) 179.

[19] W. Connell, Basic Concepts of Environmental Chemistry, Lewis Publishers, 1997.

[20] R.E. Dewhurst, J.R. Wheeler, K.S. Chummun, J.D. Mather, A. Callaghan, M. Crane, Chemosphere 47 (2002) 547.

[21] A. Parkinson, M.J. Barry, F.A. Roddick, M.D. Hobday, Water Res. 35 (2001) 3656.

[22] C. Tixier, P. Bogaerts, M. Sancelme, F. Bonnemoy, L. Twagilimana, A. Cuer, J. Bohatier, H. Veschambre, Pest. Manage. Sci. 56 (2000) 455.

[23] D.J.B. Dalzell, S. Alte, E. Asichueta, A. De la Sota, J. Etxebarria, M. Gutierrez, C.C. Hoffmann, D. Sales, U. Obst, N. Chistofi, Chemosphere 47 (2002) 535.

[24] G. Ricco, M.C. Tomei, R. Ramadori, G. Laera, Water Res. 38 (2004) 2103.

[25] M.J. Ruiz, L. López-Jaramillo, M.J. Redondo, G. Font, Bull. Environ. Contam. Toxicol. 59 (1997) 619.